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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B01D 53/36, B01J 23/56	A1	(11) International Publication Number: WO 92/05861 (43) International Publication Date: 16 April 1992 (16.04.92)
(21) International Application Number: PCT/US91/06940 (22) International Filing Date: 24 September 1991 (24.09.91) (30) Priority data: 589,470 27 September 1990 (27.09.90) US (71) Applicant: ENGELHARD CORPORATION [US/US]; 101 Wood Avenue, Iselin, NJ 08830 (US). (72) Inventor: TAUSTER, Samuel, J. ; 10 Galahad Drive, Englishtown, NJ 07726 (US). (74) Agent: MILLER, Stephen, I.; Engelhard Corporation, 101 Wood Avenue, Iselin, NJ 08830 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: CATALYST COMPOSITION CONTAINING BASE METAL OXIDE-PROMOTED RHODIUM (57) Abstract <p>A catalyst composition has a washcoat coated onto a monolithic carrier, the washcoat including a catalytic material having rhodium and a base metal oxide promoter dispersed on a ceria-promoted zirconia support, e.g., a co-formed ceria-zirconia support. A refractory metal oxide such as activated alumina may be included in the washcoat in order to enhance adhesion of it to the carrier. The presence of a rhodium-stabilizing amount, for example, 1 to 5 or 10 % by weight of the co-formed support, of the base metal oxide promoter dispersed with the rhodium on the ceria-promoted zirconia support ameliorates undesirable sintering of the rhodium. The limited amount of ceria, for example, from 1 to 25 % by weight of the weight of, for example, the conformed ceria-zirconia support, ameliorates the deleterious effect on rhodium of being intimately dispersed on a ceria-containing support. A method includes utilizing the catalyst composition for the three-way conversion of automotive engine exhaust gases.</p> <p>7.</p>		

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CATALYST COMPOSITION CONTAINING BASE METAL OXIDE-PROMOTED RHODIUM

Cross-Reference to Related Application

This application is a continuation-in-part of co-pending parent application Serial Number 07/589,470, filed September 27, 1990 in the name of Samuel J. Tauster and entitled "Catalyst Composition Containing Base Metal Oxide-Promoted Rhodium".

BACKGROUND OF THE INVENTION10 Field of the Invention

The present invention is concerned with catalysts useful for the treatment of gases to reduce contaminants contained therein, such as catalysts of the type generally referred to as "three-way conversion" or "TWC" catalysts. TWC catalysts are polyfunctional in that they have the capability of substantially simultaneously catalyzing both oxidation and reduction reactions, such as the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides in a gaseous stream. Such catalysts find utility in a number of fields, including the treatment of the exhaust gases from internal combustion engines, such as automobile and other gasoline-fueled engines.

Background and Related Art

25 In order to meet governmental emissions standards for internal combustion engine exhausts, so-called catalytic converters containing a suitable catalyst such as a TWC catalyst, are emplaced in the exhaust gas line of internal combustion engines to promote the oxidation of unburned hydrocarbons ("HC") and carbon monoxide ("CO") and the reduction of nitrogen oxides ("NO_x") in the exhaust gas. For this purpose, TWC catalysts comprising a minor amount of one or more platinum group metals distended upon a high surface area, refractory metal oxide support are well known in the art. The platinum group metal may comprise platinum or palladium, preferably including one or more of rhodium, ruthenium and iridium, especially rhodium. The refractory metal

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oxide support may comprise a high surface area alumina coating (often referred to as "activated" or "gamma" alumina) carried on a carrier such as a monolithic carrier comprising a refractory ceramic or metal honeycomb structure, as well
5 known in the art. The carrier may also comprise refractory particles such as spheres or short, extruded segments of a refractory material such as alumina.

The catalytically active materials dispersed on the activated alumina may contain, in addition to the platinum
10 group metals, one or more base metal oxides, such as oxides of nickel, cobalt, manganese, iron, rhenium, etc., as shown, for example, in C.D. Keith et al U.S. Patent 4,552,723. The activated alumina typically exhibits a BET surface area in excess of 60 square meters per gram (" m^2/g "), often up to
15 about 200 m^2/g or more. Such activated alumina is usually a mixture of the gamma and delta phases of alumina, but may also contain substantial amounts of eta, kappa and theta alumina phases.

The refractory metal oxide supports are subject to
20 thermal degradation from extended exposure to the high temperatures of exhaust gas resulting in a loss of exposed catalyst surface area and a corresponding decrease in catalytic activity. It is a known expedient in the art to stabilize refractory metal oxide supports against such thermal degradation by the use of materials such as zirconia, titania,
25 alkaline earth metal oxides such as baria, calcia or strontia or, most usually, rare earth metal oxides, for example, ceria, lanthana and mixtures of two or more rare earth metal oxides. For example, see C.D. Keith et al U.S. Patent
30 4,171,288.

TWC catalysts are currently formulated with complex washcoat compositions containing stabilized Al_2O_3 , an oxygen storage component, primarily ceria, and precious metal catalytic components. Such catalysts are designed to be effective
35 over a specific operating range of both lean of, and rich of, stoichiometric conditions. (The term "oxygen storage component" is used to designate a material which is be-

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lieved to be capable of being oxidized during oxygen-rich (lean) cycles of the gas being treated, and releasing oxygen during oxygen-poor (rich) cycles.) Such TWC catalyst compositions enable optimization of the conversion of harmful emissions (HC, CO and NO_x) to innocuous substances. Of the three precious metals, platinum, palladium and rhodium, conventionally used in TWC catalysts, rhodium is the most effective for reducing NO_x to harmless nitrogen. Unfortunately, rhodium is also the most expensive of these costly materials and, consequently, effective rhodium utilization in automotive exhaust catalysts, such as TWC catalysts, has been extensively studied.

One of the problems faced by present-day TWC catalysts is accelerated deterioration of the catalysts caused by the high operating temperatures engendered by smaller automotive engines and high speed highway driving. In addition, attempts to improve fuel economy by using air to fuel ("A/F") ratios higher than stoichiometric, and/or fuel shut-off features, generate a lean (oxygen-rich) exhaust. High temperatures and lean conditions of the exhaust gas accelerate the deterioration of platinum and rhodium catalysts, inasmuch as both platinum and rhodium are more readily sintered, and rhodium more strongly interacts with support materials such as alumina, under such conditions.

The art has devoted a great deal of effort in attempts to improve the efficiency of rhodium-containing TWC compositions. For example, U.S. Patent 4,675,308 discloses a method of effective utilization of rhodium by placing it on alumina which is segregated from ceria-containing particles, because ceria renders the rhodium less active. Other attempts to segregate rhodium from ceria are disclosed in U.S. Patent 4,806,519; Japanese Patent application 88-326823/46 (J63240947A) of Nissan Motor KK (10.02.87-JP-027383), and in Japanese Patent publication JP63 77,544 (88 77,544). It is known to utilize zirconia as a support for rhodium, e.g., U.S. Patent 4,233,189 teaches the use of non-alumina supports such as zirconia for rhodium. Similarly, U.S. Patent

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4,492,769 discloses palladium and other platinum group metals dispersed on a zirconia support together with base metals. The use of rhodium dispersed on zirconia is also disclosed in U.S. Patents 4,233,189 and 4,405,506, and Japanese Patent 6-1,157,347A, dated December 28, 1984. However, zirconia has certain disadvantages including a lower surface area than gamma alumina and the fact that zirconia itself is not a thermally stable support. Zirconia undergoes a phase transition between its monoclinic crystalline structure and its more stable tetragonal crystalline structure over a wide temperature range; such transition causes drastic sintering of the associated precious metals.

There remains a need for improved stabilization against thermal degradation of rhodium-containing catalysts carried on zirconia supports. An attempt at obtaining such stabilization is disclosed in Nippon Shokubai Japanese Patent application HEI 1-93045 of Kitaguchi et al, filed April 14, 1989 and claiming priority of applications Showa 63-90310 (April 14, 1988) and Showa 63-90311 (April 14, 1988). This application discloses a catalyst comprising rhodium and, optionally, platinum and/or palladium, dispersed on a support comprising ceria stabilized with zirconia or yttria or calcia, and a refractory metal oxide such as alumina. The rhodium is stated to be supported on the alumina in a high concentration and in a relatively large rhodium particle size. The zirconia is stabilized with the ceria (or yttria or calcia) by impregnation of zirconia with, for example, a solution of cerium nitrate, followed by calcination. The rhodium is supported on at least one of the stabilized cerium oxide and the refractory inorganic oxide.

SUMMARY OF THE INVENTION

Generally, in accordance with the present invention, there is provided a catalyst composition comprising a catalytic material in which rhodium is dispersed on a ceria-promoted zirconia support, such as a co-formed (as defined below) ceria-zirconia support, with the rhodium being sta-

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bilized against thermal degradation by a base metal oxide promoter.

Specifically, in accordance with the present invention, there is provided a catalyst composition comprising a carrier on which is disposed a washcoat of a catalytic material. The catalytic material comprises a ceria-promoted support, e.g., a co-formed ceria-zirconia support, having dispersed thereon a catalytically effective amount of rhodium and a rhodium-stabilizing amount of a base metal oxide promoter. The ceria content of the ceria-promoted zirconia support (which in all cases described herein optionally may be a co-formed ceria-zirconia support) may comprise, for example, from about 5 to 25% by weight of the weight of the ceria-promoted zirconia support.

In one aspect of the present invention, the base metal oxide promoter dispersed on the ceria-promoted zirconia support may be present in an amount of from about ~~1 to~~ 1.0%, preferably ~~1 to~~ 5%, by weight of the weight of the ceria-promoted zirconia support, and is selected from the group consisting of ~~calcium oxide, copper oxide, iron oxide, lanthanum oxide, magnesium oxide, manganese oxide, nickel oxide and tin oxide.~~

In accordance with another aspect of the present invention, the washcoat further comprises a refractory metal oxide, e.g., alumina.

In a specific aspect of the present invention, the base metal oxide comprises one or both of ~~nickel oxide and magnesium oxide.~~

The method aspect of the invention provides a method for treating a gas (such as the exhaust gas of a gasoline-fueled automobile engine) containing noxious components comprising one or more of carbon monoxide, hydrocarbons and nitrogen oxides by converting at least some of the noxious components into innocuous substances, the method comprising contacting the gas under conversion conditions, for example, at an initial temperature of from about 250°C to 500°C, with a catalyst composition comprising a carrier on which is dis-

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posed a washcoat comprising a catalytic material as described above.

As used herein and in the claims, the following terms have the indicated meanings.

5 A "rhodium-stabilizing amount" of the base metal oxide promoter means an amount of the promoter which significantly ameliorates the catalytic de-activation which an otherwise identical rhodium-containing catalyst lacking the base metal oxide promoter would sustain under identical conditions of
10 use, due to formation of stable rhodium oxides from the catalytic rhodium metal.

 The term "innocuous substances" refers to the CO_2 and H_2O formed by oxidation of CO and hydrocarbons and the N_2 formed by reduction of nitrogen oxides. For example, treat-
15 ment of an automobile engine exhaust gas with a suitable TWC catalyst under conversion conditions will convert at least some of the carbon monoxide ("CO"), nitrogen oxides ("NOx") and unburned hydrocarbons ("HC") to innocuous substances, as defined herein.

20 The term "ceria-promoted zirconia support" means a zirconia support material with which ceria is intimately combined, for example, by having a coating of ceria deposited on the zirconia particles, or by impregnating zirconia particles with a solution or liquid dispersion of a cerium salt
25 or other cerium compound decomposable to the oxide, followed by drying and calcination to convert the cerium compound to ceria. The term "ceria-promoted zirconia support" also includes, as a special case thereof, a co-formed ceria-zirconia support as defined below.

30 The term "co-formed ceria-zirconia support" and the term "co-formed" as used with respect to the co-formed ceria-zirconia support material, means that the ceria is distributed substantially throughout the entire matrix of the zirconia particles as will occur, for example, when the
35 cerium oxide and zirconium oxide, or predecessors thereof, are co-precipitated or co-gelled. The defined term is intended to distinguish the material from that obtained in a

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situation in which ceria is merely dispersed on or near the surface of the zirconia particles, leaving the core of the particles largely or entirely free of the ceria. The latter situation would occur, for example, if a solution of a soluble cerium salt, e.g., cerium nitrate, were impregnated onto zirconia particles and the resulting impregnated particles were dried and calcined to convert the cerium nitrate to ceria. The material resulting from such treatment fits the definition of a "ceria-promoted zirconia support" but is not a co-formed ceria-zirconia support.

Reference to a component (such as rhodium or the base metal oxide promoter) being "dispersed" on a support or reference to "dispersion" or "dispersal" in the same context, means that the component was impregnated onto the support from a solution of the component or of a precursor of the component. This is intended to distinguish the "dispersed" component from the situation in which the component is introduced in "bulk", that is, in fine particulate form. For example, if the base metal oxide promoter is nickel oxide, it is "dispersed" on the support by impregnating the support with a solution of nickel nitrate and then drying and calcining the support to convert the impregnated nickel salt to nickel oxide. The defined terms thus exclude incorporation of the nickel oxide into the support in the form of fine particles of solid nickel oxide.

DETAILED DESCRIPTION OF THE INVENTION, INCLUDING PREFERRED EMBODIMENTS THEREOF

The present invention provides for the dispersal of a rhodium catalytic component on a zirconia support which is promoted, e.g., co-formed, with ceria, and therefore is contrary to those teachings of the prior art which teach that ceria has a de-activating effect on the performance of rhodium when the two are in contact. The invention is accomplished by dispersing a base metal oxide promoter together with the dispersed rhodium on a ceria-promoted zirconia support. Without wishing to be bound to any particular theory,

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it is believed that the base metal oxide suppresses the rhodium sintering which has been known to occur under high temperature oxidizing conditions in the rhodium-containing catalytic materials of the prior art. It is speculated that
5 under such conditions, the base metal oxide forms a complex with the rhodium oxide, thereby "anchoring" the rhodium and preventing the growth of uncomplexed rhodium oxides which destroy the effectiveness of the catalyst. In a preferred case, it is believed that by co-forming the ceria with the
10 zirconia (as opposed to merely dispersing the ceria onto particles of zirconia), and by limiting the amount of ceria in the co-formed support, all as described below, the undesired adverse effect of ceria on rhodium is avoided or further significantly attenuated.

15 Generally, the catalyst compositions of the present invention are free of bulk ceria, at least in amounts which would adversely affect the activity of the rhodium catalyst. Preferably, the catalyst compositions are substantially free of bulk ceria and, more preferably, are substantially free
20 of ceria either in bulk form (fine particles of ceria) or in dispersed form, except for the ceria used to promote the zirconia support, e.g., the ceria forming part of the co-formed ceria-zirconia support.

It should be understood that the promoting ceria, e.g.,
25 the ceria which is co-formed with the zirconia, may (but need not) contain small but significant quantities of other rare earth metal oxides as is the case with commercial grades of ceria. Although the present invention embraces ceria-promoted zirconia supports generally, the co-formed
30 ceria-zirconia support is, as indicated above, preferred and the following description will refer thereto. However, it should be understood that except where specifically otherwise stated the descriptions generally apply to ceria-promoted supports as well. In preparing a catalyst composition
35 according to this invention, a first catalytic component is prepared by dispersing rhodium metal on a co-formed ceria-zirconia support. The support may be formed by co-precipi-

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tating or co-gelling zirconia with ceria or by other suitable methods to produce a frit in which ceria is bound in, and distributed substantially throughout, the zirconia component. The amount of ceria present in the co-formed support should be limited to between about 1 to 25% by weight of the weight of the co-formed ceria-zirconia support, preferably from about 5 to 20% by weight, e.g., 12% by weight. The balance of the co-formed support is substantially or entirely zirconia, which accordingly comprises about 99 to 75% by weight of the co-formed ceria-zirconia support, preferably about 95 to 80%.

It should be understood that neither the ceria-promoted zirconia support itself generally nor the co-formed ceria-zirconia support itself specifically form any part of the present invention. For example, the nature of co-formed ceria-zirconia supports and their use in a catalyst composition are the subject of a prior and co-pending Japanese Patent Application 145491/89, which describes a catalyst for exhaust gas purification in which platinum group metal components including rhodium are used in a washcoat containing a co-formed ceria-zirconia support. Specifically, catalyst compositions including platinum group metals such as platinum and rhodium dispersed on alumina are admixed with cerium oxide, with the co-formed ceria-zirconia material and optionally with a zirconium compound to form a washcoat slurry. The co-formed ceria-zirconia support of the Japanese application is described as being produced by coprecipitation from a solution of suitable zirconium and cerium compounds. The co-formed ceria-zirconia support produced by coprecipitation is said to retain at high temperatures a quasi-stable cubic crystal structure which is said to have catalytic activity of its own. This is stated to contrast with the thermal degradation of zirconium oxide from a quasi-stable cubic system to a catalytically inactive monoclinic crystalline configuration. The co-formed ceria-zirconia support is described as having a specific surface area of from about 10 to 150 square meters per gram, preferably

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from about 50 to 80 square meters per gram. The weight ratio of cerium oxide to zirconium oxide in the co-formed ceria-zirconia support may be from about 1 part ceria to 99 parts zirconia, to about 25 parts ceria to 75 parts zirconia. Stated otherwise, the ceria may comprise from about 1% to about 25% by weight of the combined weight of the co-formed ceria-zirconia.

In accordance with the teachings of the present invention, ~~rhodium and a base metal cation are dispersed onto the co-formed ceria-zirconia support.~~ This may be accomplished in a conventional manner, for example, by impregnating the co-formed support with a solution of an appropriate rhodium salt, e.g., rhodium nitrate, and with the nitrate salt precursor of a suitable base metal oxide promoter. A single impregnation solution may contain both a rhodium salt and a base metal salt or separate solutions of a rhodium salt and a base metal salt may be utilized in successive impregnations. The order of impregnation is not important and the rhodium salt solution and base metal salt solution may be impregnated onto the co-formed support in any order. However, it is more efficient to conduct a single impregnation and single drying and calcining to impregnate both the rhodium and base metal precursors, instead of separate impregnation(s), drying and calcining cycles for each component. To that extent, it is preferred to utilize a single solution containing both a rhodium salt and a base metal salt dissolved therein. In any case, the co-formed support, after being impregnated with both the rhodium and base metal oxide precursor salts, is dried and calcined in the conventional manner. For example, the impregnated co-formed support may be dried in air for about 2 to 24 hours at 110°C followed by ~~calcining~~ in air for about 1 to 24 hours at a temperature of about ~~350 to 550°C~~. Calcining results in the decomposition of the rhodium salt into rhodium oxide, and of the base metal salt into the base metal oxide. The resulting calcined composition may then be milled, as well known in the art, so that at least 90% of the particles have a diameter of less

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than 12 microns. The impregnated co-formed support comprises active catalyst components and may be milled with a bulk extender such as alumina of approximately the same particle size as the active catalyst components and in a weight proportioned to the catalyst components to produce a "wash-coat" having an appropriate rhodium loading. Alumina is preferred as the bulk extender because it also has a binding effect, which helps to secure the washcoat onto the surface of the substrate onto which the washcoat is applied. However, other extenders in lieu of or in addition to alumina may be used as is known in the art, for example, silica, titania, zirconia and the like. In addition, other catalytic metals, including precious metals such as platinum and/or palladium may be dispersed throughout the washcoat and these, especially platinum or palladium, may conveniently be dispersed on the alumina or other refractory metal oxide employed as the extender. Here too, alumina is preferred and, the alumina used, or the alumina resulting from a final calcining step or from initial use of the catalyst, will preferably be "activated alumina", i.e., a high surface area alumina comprising primarily gamma alumina, although other phases such as theta and eta alumina may be present. The resultant washcoat, comprising a mixture of alumina (and/or other extender) and the impregnated co-formed ceria-zirconia particles is coated onto a carrier, such as a cordierite honeycomb, in a manner well known in the art, and is then dried and calcined to provide the finished catalyst.

The specific method of making the catalyst is not critical with respect to the sequence of impregnating the solids with the rhodium and, optionally, other precious metal solution(s) and with the base metal solution(s). Thus, the co-formed ceria-zirconia support and, optionally, the refractory metal oxide may be admixed prior to impregnation with the solution or solutions of base metal salts so that both the refractory metal oxide and the co-formed ceria-zirconia support are impregnated with the base metal compound which is eventually converted into the base metal oxide. In such

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case, an amount of the base metal salt will be used to provide the desired loading of base metal oxide promoter on the co-formed ceria-zirconia support because, depending on the proportion of refractory metal oxide to co-formed ceria-zirconia support, a greater or lesser proportion of the base metal solution will be taken up by the refractory metal oxide. In another alternative, the co-formed ceria-zirconia support and, optionally, the refractory metal oxide may be deposited onto a substrate and calcined to form a coating, and the calcined coating is then impregnated with the base metal solution. Conceivably, any of these approaches could also be taken with the rhodium salt solution.

The relative concentrations of rhodium salt and base metal salt in the impregnating solution or solutions are selected to provide the desired overall loadings of base metal oxide promoter and rhodium in the finished catalyst composition. The amount of base metal oxide promoter provided is typically from about 1 to 10% by weight of the weight of the co-formed ceria-zirconia support itself (not counting the weight of the promoter, catalytic metals or other components dispersed on the co-formed support), dry basis, with the base metal oxide promoter measured as the oxide. However, it should be understood that it is within the purview of the present invention to introduce larger amounts of the base metal oxide precursor throughout the entire catalytic material or washcoat. Thus, it may be desired to prepare the catalytic material by introducing both the alumina or other extender or binder material as well as the co-formed ceria-zirconia support material into a solution containing a dissolved base metal salt so that, in the finished catalyst, the base metal oxide is dispersed throughout substantially the entire catalytic material. The preferred amount of base metal oxide promoter, that is, 1 to 10% by weight, preferably 1 to 5% by weight, of the weight of the co-formed ceria-zirconia support, is the amount of base metal oxide promoter dispersed on the co-formed ceria-zirconia support itself. The amount, if any, of base metal oxide on the alumi-

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na or other components in the washcoat is not counted towards the preferred 1 to 10% range. It is believed that an excessive amount of the base metal oxide promoter dispersed on the co-formed ceria-zirconia support itself may prevent the reduction of the "anchored" rhodium oxides to rhodium metal and thus be detrimental to catalytic activity.

All percentages by weight given herein and in the claims are calculated on a dry basis with the component (ceria, zirconia or the base metal oxide promoter as the case may be) calculated as the oxide. It will be appreciated that some of the base metal oxides may exist in different valence states and that the valence states may change during use of the catalyst compositions. However, for purposes of calculating the weight percentage of components of the catalyst compositions, the formulae given in TABLE I below for the base metal oxides are used. Ceria and zirconia are taken as CeO_2 and ZrO_2 , respectively.

Example 1

A. A series of catalyst compositions according to this invention is prepared as follows. A co-formed ceria-zirconia support is obtained by co-precipitating ceria and zirconia from a solution of both zirconium and cerium soluble compounds. The result is a co-formed ceria-zirconia support comprising about 12% by weight ceria and about 88% by weight zirconia. Separate portions of the co-formed ceria-zirconia support were then impregnated with an aqueous solution of rhodium nitrate and the nitrate salt of respective ones of the base metal cations listed in TABLE I, except in the case of tin for which tin chloride (SnCl_4) was used. That is, each solution used to prepare a catalyst sample exemplary of the present invention contained both rhodium nitrate and a base metal salt dissolved therein. The metal salt solutions were employed at concentrations to provide the rhodium and base metal loadings set forth in TABLE I. Each of the metal solution-impregnated portions of co-formed support were dried in air at 100°C for 1 hour and then calcined in air

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for 2 hours at 450°C.

B. For comparison, portions of co-formed ceria-zirconia support were prepared in the same manner as in Part A except that the base metal nitrate salt was excluded from the rhodium nitrate solution.

C. The dried and calcined rhodium-impregnated co-formed ceria-zirconia compositions obtained from Parts A and B respectively are separately milled so that at least 90% of the resulting particles have a diameter of less than 12 microns. Each milled component is separately combined with milled alumina of approximately the same particle size (about 90% of the alumina particles having a diameter of less than 12 microns) in a 1:1 ratio (dry solids weight basis) to form a washcoat slurry. The slurries were coated onto respective cordierite honeycomb cores which were then dried in air at 110°C and calcined at 450°C for 2 hours. The resulting concentration of rhodium in the washcoat was 0.39% by weight of the co-formed ceria-zirconia support. The total washcoat loading was about 1.2 grams per cubic inch of the carrier. The choice (or exclusion) of base metal salt and the corresponding base metal oxide and the amount thereof (or lack thereof) in the catalyst composition, when present, is shown in TABLE I below. The various samples are identified as Samples 1A, 1B, 1C, 2A, 2B, etc..

Example 2

Catalyst compositions prepared according to Example 1 were loaded into testing chambers and subjected to a 50 hour aging cycle at 900°C inlet gas temperature. The cycle included a simulated fuel shut-off for five seconds every minute. The fuel shut-off simulation was attained by introducing air into the exhaust gas ahead of the catalyst to provide a lean gas to the catalyst. The engine utilized for the aging burned a commercially available normal hydrocarbon gasoline fuel having a lead content of about 3 milligrams Pb per gallon of fuel. The compositions were then tested, first by determining the "light-off" temperature (defined

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below) of the catalysts in a perturbed flow of engine exhaust gases generated by combusting a stoichiometric air to fuel ratio combustion mixture, and then under "sweep" testing conditions at ± 0.3 A/F Ratio Units, 2 Hz, 450°C, and a space velocity of 80,000 volumes of gas per volume of catalyst per hour. All catalyst composition samples were tested in the exhaust gas generated by an engine burning a commercial unleaded gasoline containing not more than 5 milligrams per gallon Pb. The performance of the various compositions is shown in TABLE I, below. All comparisons are between catalysts that have been aged and tested together under the same conditions. The temperatures listed under T_{50} (light-off temperatures) are the average temperature in degrees Centigrade for conversion to CO_2 and/or H_2O of 50% of the content of, respectively, hydrocarbons and carbon monoxide in the test gas. The temperature of the exhaust gas was increased at a rate of approximately 20°C per minute until the light-off temperature was attained.

In TABLE I, "Smpl." means Sample, "% Prom." means the percent by weight of base metal promoter dispersed on the co-formed ceria-zirconia support of the catalyst composition sample and " T_{50} " is the light-off temperature. The term "% Conversion" means the percentage of the pollutant (HC, CO and NO_x) in the untreated exhaust gas which is converted to innocuous substances, i.e., CO_2 , H_2O and/or N_2 . The definition of "Lean" and "Rich" is based on the definition of the stoichiometric air to fuel weight ratio for gasoline as being 14.65 parts by weight air to parts by weight gasoline. The air to fuel ratio ("A/F") is referred to in terms of deviation, measured in A/F Units, from the stoichiometric baseline of 14.65. Thus, an A/F of 14.15 (a rich A/F) is 0.5 A/F Units less than stoichiometric ($14.65 - 0.5 = 14.15$), and is described as -0.5 A/F Unit. Conversely, an A/F of 15.15 (a lean A/F) is described as +0.5 A/F Unit ($14.65 + 0.5 = 15.15$). As used in TABLE I, "Rich" means -0.2 A/F Units (or a 14.45 A/F Ratio), "Lean" means +0.2 A/F Units (or a 14.85 A/F Ratio) and "Stoich." means a stoichio-

metric air-to-fuel ratio (14.65) of the combustion mixture fed to the engine which generates the gas being treated. The rhodium content of the catalyst composition samples is given in grams of rhodium per cubic foot of catalyst volume ("g/ft³ Rh").

TABLE I

10	Smpl.	% Prom.	g/ft ³ Rh	T50	Rich			Stoich.			Lean		
					HC	CO	Nox	% Conversion			HC	CO	Nox
								HC	CO	Nox			
	1A	none	4.2	434	40	18	71	63	63	77	51	85	33
	1B	3% MgO	4.4	413	46	25	81	68	70	81	53	89	34
15	1C	2% N10	4.1	405	54	32	89	71	74	82	56	92	33
	2A	none	4.0	421	64	43	82	83	74	65	86	98	34
	2B	3%	4.0	401	66	44	88	84	78	66	86	98	34
20	3A	La ₂ O ₃ none	4.4	381	64	39	97	74	91	77	61	97	32
	3B	3%	4.5	375	65	38	97	76	96	78	60	97	32
	4A	Mn ₃ O ₄ none	4.2	384	65	29	94	75	82	80	64	94	35
	4B	5%	4.2	346	68	32	98	81	93	84	68	98	30
25	5A	MgO none	3.7	400	69	36	98	74	84	88	64	93	70
	5B	0.4% CuO	4.0	395	72	38	98	76	90	88	63	95	70
	5C	4% N10	3.4	396	65	37	96	71	82	87	62	89	68
30	6A	none	4.0	402	60	37	95	73	84	81	60	93	35
	6B	1% MgO	4.1	401	60	38	96	73	83	80	60	94	38
	7A	none	4.4	407	51	27	86	68	73	75	54	86	28
35	7B	2% SnO ₂	4.0	391	54	29	93	75	86	84	56	91	30

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TABLE I (CONT.)

	Smpl.	% Prom.	g/ft ³ Rh	T50	Rich			Stoich.			Lean		
					% Conversion			% Conversion			% Conversion		
					HC	CO	Nox	HC	CO	Nox	HC	CO	Nox
5	8A	none	4.2	406	52	38	91	72	90	81	58	87	30
	8B	1%	4.3	396	52	37	87	71	87	80	57	84	28
		MgO											
	8C	5%	4.2	381	58	41	95	75	94	83	58	89	29
10		MgO											
	9A	none	4.2	365	53	36	96	79	91	86	63	86	27
	9B	1%	3.9	366	51	30	97	80	92	86	64	88	26
		NiO											
	9C	2%	4.0	363	53	36	97	80	94	86	63	90	26
15		NiO											
	10A	none	4.3	407	48	30	87	70	80	86	58	85	36
	10B	0.7%	4.1	385	58	29	96	79	86	94	65	93	36
		CuO											
	11A	none	4.0	365	49	38	95	78	96	90	64	91	31
20	11B	2%	4.2	347	49	39	96	77	96	93	64	92	32
		Fe ₂ O ₃											
	11C	5%	4.2	342	54	40	96	80	97	93	64	90	29
		CaO											
	11D	5%	4.2	342	52	38	97	80	96	91	65	94	30
25		La ₂ O ₃											

The comparison of Comparative Sample 1A with Samples 1B and 1C show that the latter two exhibit a significantly lower light-off temperature than does Sample 1A, which contains no base metal oxide promoter. A lower light-off temperature of course means that the catalyst is more active at lower temperatures, which enhances conversion of pollutants during cold start-up periods of engine operation. Further, the presence of 3 weight percent MgO and 2 weight percent NiO in, respectively, Samples 1B and 1C significantly improved the percentage conversion of all three pollutants (HC, CO and NOx) under both rich and stoichiometric conditions, as

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compared to Comparative Sample 1A.

Sample 2B shows a significant reduction in light-off temperature and substantially increased conversion of NO_x under rich operating conditions, and of CO under stoichiometric operating conditions as compared to Comparative Sample 2A.

With respect to Comparative Sample 3A, Sample 3B shows significantly improved activity for CO reduction at stoichiometric conditions.

The incorporation of 5 weight percent MgO in Sample 4B shows, as compared to Comparative Sample 4A, significantly lowered light-off temperature and improved conversion of NO_x under rich conditions, improved conversion of all three pollutants under stoichiometric conditions, and of HC and CO under lean conditions. However, significantly decreased activity for NO_x under lean conditions was observed.

Sample 5B, containing 0.4 percent CuO, shows significantly improved conversion of CO at stoichiometric conditions as compared to Comparative Sample 5A. However, in this particular test, the inclusion of 4 weight percent NiO in Sample 5C did not show a significant improvement in activity under these particular test conditions. However, the efficacy of NiO as a base metal oxide promoter in the catalyst compositions of the present invention is amply demonstrated by Samples 9A-C, discussed below, as well as in Samples 1A and 1C, as discussed above.

The addition of 1 percent by weight MgO in Sample 6B did not show significantly improved activity relative to Comparative Sample 6A. However, the efficacy of MgO in somewhat greater amount is amply demonstrated by Sample 8C, discussed below and in Samples 1A and 1B, as discussed above.

A comparison of Comparative Sample 7A with Sample 7B shows that the incorporation of 2 percent by weight SnO₂ provides a significantly lower light-off temperature and increased conversion of NO_x under rich conditions, increased conversion of all three pollutants under stoichiometric con-

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ditions, and increased conversion of CO under lean conditions.

5 The addition of 5 weight percent MgO in Sample 8C shows significantly reduced light-off temperature and increased conversion of HC and NOx under rich conditions, and increased conversion of CO under stoichiometric conditions.

10 Similarly, Samples 9B and 9C as compared to Comparative Sample 9A shows that the addition of 2 percent NiO significantly improves conversion of CO under lean conditions and marginally improves conversion of CO under stoichiometric conditions, while the addition of 1 percent by weight NiO in Sample 9B had the adverse effect of decreasing the conversion of CO under rich conditions.

15 A comparison of Sample 10B to Comparative Sample 10A shows that the addition of 0.7 percent by weight CuO significantly improved, that is, reduced, the light-off temperature as well as providing significant increases in conversion of all pollutants under all three conditions except for CO under rich conditions and NOx under lean conditions.

20 Finally, reference to Samples 11A through 11D shows that the indicated base metal oxide promoters in Samples 11B, 11C and 11D significantly reduced light-off temperature. In addition, the 2 percent by weight Fe_2O_3 of Sample 1B marginally improved conversion of NOx at stoichiometric conditions, the 5 percent by weight CaO incorporated in Sample 11C significantly improved conversion of HC under rich conditions and marginally improved conversion of NOx under stoichiometric conditions, and the 5 percent by weight La_2O_3 incorporated into Sample 11D marginally improved conversion of HC under rich conditions and CO under lean conditions.

Example 3

35 Two catalyst compositions were prepared using techniques similar to those of Example 1 to produce catalyst compositions in which the washcoat is provided as two discrete bottom and top layers on the substrate. Thus, the substrates comprising cordierite honeycomb cores were ini-

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tially coated with a slurry comprising approximately 67% by weight (dry solids basis) of activated alumina and 33% by weight of bulk ceria, i.e., fine particles of cerium oxide. The platinum was impregnated with a platinum hydroxide methylethanolamine solution so that approximately 2% by weight of the combined impregnated alumina and bulk ceria comprised platinum. After drying and calcining the bottom coat, the coated cordierite substrate was provided with a top coat by being dipped into a slurry prepared as follows. Rhodium nitrate was utilized to impregnate activated alumina and the impregnated alumina was mixed with a quantity of co-formed ceria-zirconia support in which ceria comprised about 12% by weight of the weight of the co-formed support. The quantity of zirconyl acetate was then introduced to the slurry of alumina and co-formed ceria-zirconia support particles so that the zirconyl acetate impregnated both the alumina and the co-formed ceria-zirconia particles. Excess slurry was blown from the twice-coated core which was then dried and calcined to provide an outer or top coat layer comprising approximately 38% by weight alumina, approximately 53% by weight of co-formed ceria-zirconia support, approximately 9% by weight zirconia and approximately 0.42% by weight rhodium. The inner or bottom coat comprises about 68% by weight of the total weight of washcoat (catalytic material) and the top coat comprised about 32% by weight. Additionally, in order to produce the base metal oxide promoted version of this catalyst in accordance with the invention (Sample 12B), nickel nitrate is added to the top coat slurry in an amount sufficient so that, if all of the nickel were to migrate to the co-formed ceria-zirconia support, it would amount to 17.8% by weight of the co-formed ceria-zirconia support. Of course, not all of the nickel migrates to the co-formed support and some of it will migrate to the alumina particles contained in the top coat slurry. Because of the surface properties of alumina as compared to those of the co-formed ceria-zirconia support and other factors, only about 10 to 25% of nickel oxide can be expected to end up dispersed onto

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the co-formed ceria-zirconia support. Therefore, in Sample 12B the amount of nickel oxide promoter dispersed on the co-formed ceria-zirconia support is estimated at from about 1.8 to 4.5% by weight of the weight of co-formed ceria-zirconia support.

The total loading of precious metal (platinum plus rhodium) on the catalyst Samples 12A and 12B is 40 grams per cubic foot, with the platinum and rhodium being present in a weight ratio of 5 parts platinum to 1 part rhodium.

Example 4

The catalyst compositions prepared according to Example 3 were loaded into testing chambers and subjected to an aging cycle similar to that described in Example 2 except that an inlet gas temperature of 850°C and an actual fuel shut-off was utilized, instead of the simulated fuel shut-off employed in Example 2. The fuel shut-off was continued for about five seconds every minute. The abbreviations of TABLE II have the same meaning as those given above for TABLE I. Aging and testing of the catalyst samples were the same as those described above in Example 2, except that the gasoline burned to generate the exhaust gas contained 12 milligrams Pb per gallon and the sweep testing conditions were carried out at ± 0.5 A/F Ratio Units at 350°C and a space velocity of 135,000 volumes of gas (measured at standard conditions of temperature and pressure) per volume of catalyst per hour. Data was not taken at lean conditions.

TABLE II

Smpl.	Prom.	Rh	T50	Rich			Stoich.		
				% Conversion					
				HC	CO	Nox	HC	CO	Nox
12A	---	6.7	371	11	13	30	51	42	46
12B	8.9	6.7	359	23	20	50	68	57	58

The data of TABLE II shows significant reduction in

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light-off temperature for the nickel oxide promoted catalyst as compared to the unpromoted catalyst and significantly better conversions of the noxious components to innocuous substances attained.

5 The suitability of ceria-promoted zirconia supports other than co-formed ceria-zirconia supports for the purposes of the present invention is indicated by tests of comparable, but different, catalyst compositions containing platinum and rhodium catalytic components dispersed on
10 ceria-promoted zirconia supports obtained by impregnating zirconia particles with a solution of cerium nitrate. The impregnated particles were then calcined to decompose the cerium nitrate to ceria. The catalyst was aged and tested on the exhaust gas of a stock Nissan GLD engine. The ceria-
15 promoted zirconia support showed good durability and the catalyst showed good activity, indicating that ceria-promoted zirconia supports generally, including those which are not co-formed, are suitable for purposes of the present invention.

20 While the invention has been described in detail with respect to specific embodiments thereof, it will be appreciated that variations to the invention may be made which will nonetheless lie within the sphere and scope of the invention and are intended to be embraced by the appended claims.

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THE CLAIMS

What is claimed is:

1. A catalyst composition comprising a carrier on which is disposed a washcoat of catalytic material comprising a ceria-promoted zirconia support having dispersed thereon (i) a catalytically effective amount of rhodium and (ii) a rhodium-stabilizing amount of a base metal oxide promoter.

2. The catalyst composition of claim 1 wherein the ceria-promoted zirconia support comprises a co-formed ceria-zirconia support.

3. The catalyst composition of claim 2 wherein the co-formed ceria-zirconia support comprises from about 1 to 25% by weight of ceria.

4. The catalyst composition of claim 1, claim 2 or claim 3 wherein the base metal oxide promoter dispersed on the ceria-promoted zirconia support is present in an amount of from about 1 to 10% by weight of the weight of the ceria-promoted zirconia support.

5. The catalyst composition of claim 4 wherein the ceria-promoted zirconia support comprises a co-formed zirconia support.

6. The catalyst composition of claim 4 wherein the base metal oxide promoter is present in an amount of from about 1 to 5% by weight of the weight of the ceria-promoted zirconia support.

7. The catalyst composition of claim 6 wherein the ceria-promoted zirconia support comprises a co-formed zirconia support.

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8. The catalyst composition of claim 1, claim 2 or claim 3 wherein the washcoat further comprises a refractory metal oxide.

9. The catalyst composition of claim 8 wherein the refractory metal oxide comprises alumina.

10. The catalyst composition of claim 1, claim 2 or claim 3 wherein the base metal oxide is selected from the group consisting of calcium oxide, copper oxide, iron oxide, lanthanum oxide, magnesium oxide, manganese oxide, nickel oxide and tin oxide.

11. The catalyst composition of claim 10 in which the base metal oxide promoter dispersed on the co-formed ceria-zirconia support is present in an amount of from about 1 to 10% by weight of the weight of the co-formed ceria-zirconia support.

12. The catalyst composition of claim 1, claim 2 or claim 3 wherein the base metal oxide comprises one or both of nickel oxide and magnesium oxide.

13. A catalyst composition comprising a carrier on which is disposed a washcoat of a catalytic material comprising a ceria-promoted zirconia support in which ceria comprises from about 1 to 25% by weight of the weight of the support, and the support has dispersed thereon (i) a catalytically effective amount of rhodium and (ii) a base metal oxide present in an amount of from about 1 to 10% by weight of the weight of the ceria-promoted zirconia support.

14. The catalyst composition of claim 13 wherein the ceria-promoted zirconia support comprises a co-formed ceria-zirconia support.

15. The catalyst composition of claim 13 or claim 14

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wherein the base metal oxide promoter is present in an amount of from about 1 to 5% by weight of the weight of the co-formed ceria-zirconia support.

16. The catalyst composition of claim 13 or claim 14 wherein the washcoat further comprises a refractory metal oxide.

17. The catalyst composition of claim 16 wherein the refractory metal oxide comprises alumina.

18. The catalyst composition of claim 13 or claim 14 wherein the base metal oxide is selected from the group consisting of calcium oxide, copper oxide, iron oxide, lanthanum oxide, magnesium oxide, manganese oxide, nickel oxide and tin oxide.

19. The catalyst composition of claim 13 or claim 14 wherein the base metal oxide comprises one or both of nickel oxide and magnesium oxide.

20. The catalyst composition of any one of claims 1, 2, 3, 13 or 14 further including one or both of platinum and palladium dispersed in the washcoat.

21. The catalyst composition of claim 16 further including one or both of platinum and palladium dispersed on the refractory metal oxide.

22. A method for treating a gas containing noxious components comprising one or more of carbon monoxide, hydrocarbons and nitrogen oxides by converting at least some of the noxious components into innocuous substances, the method comprising contacting the gas under conversion conditions with a catalyst composition comprising a carrier on which is disposed a washcoat of a catalytic material, wherein the catalytic material comprises a ceria-promoted zirconia sup-

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port having dispersed thereon (i) a catalytically effective amount of rhodium and (ii) a rhodium-stabilizing amount of a base metal oxide promoter.

23. The method of claim 22 wherein the ceria-promoted zirconia support is a co-formed ceria-zirconia support.

24. The method of claim 22 or claim 23 wherein the base metal oxide is selected from the group consisting of calcium oxide, copper oxide, iron oxide, lanthanum oxide, magnesium oxide, manganese oxide, nickel oxide and tin oxide and the base metal oxide promoter dispersed on the ceria-zirconia support is present in the amount of from about 1 to 10% by weight of the weight of the co-formed ceria-zirconia support and the rare earth metal oxide comprises from about 1 to 25% by weight of the weight of co-formed ceria-zirconia support.

25. The method of claim 22 or claim 23 wherein the gas is at a temperature of from about 250 to 500°C when it is initially contacted with the catalyst.

26. The method of claim 22 or claim 23 wherein the wash-coat further comprises a refractory metal oxide and includes one or both of platinum and palladium dispersed therein.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/06940

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B01D53/36; B01J23/56		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B01D ; B01J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 326 845 (DEGUSSA) 9 August 1989 see claims 1,2	1,10,13
P,A	EP,A,0 427 493 (ENGELHARD CORPORATION) 15 May 1991 see claims	1-5, 13-15, 21,22, 25,26
A	FR,A,2 449 475 (DEGUSSA) 19 September 1980	
A	EP,A,0 125 565 (NIPPON SHOKUBAI KAGAKU KOGYO) 21 November 1984	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 JANUARY 1992	27. 01. 92	
International Searching Authority	Signature of Authorized Officer	
EUR PEAN PATENT FFICE	BOGAERTS M. L. M.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9106940
SA 51979**

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The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0326845	09-08-89	DE-C- 3803122	13-07-89
		JP-A- 1228546	12-09-89
EP-A-0427493	15-05-91	JP-A- 3154635	02-07-91
FR-A-2449475	19-09-80	DE-A- 2907106	04-09-80
		CA-A- 1125265	08-06-82
		GB-A, B 2048101	10-12-80
		JP-C- 1267578	10-06-85
		JP-A- 55157327	08-12-80
		JP-B- 59045416	06-11-84
		SE-B- 445302	16-06-86
		SE-A- 8001370	06-10-80
		SU-A- 1170958	30-07-85
		US-A- 4294726	13-10-81
EP-A-0125565	21-11-84	JP-C- 1406311	27-10-87
		JP-A- 59209646	28-11-84
		JP-B- 62014337	01-04-87
		JP-C- 1406313	27-10-87
		JP-A- 59230639	25-12-84
		JP-B- 62014338	01-04-87
		CA-A- 1213874	11-11-86
		US-A- 4504598	12-03-85

FORM PCT/89